Ion rotational distributions for near-threshold photoionization of H2O

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COMMUNICATIONS

Ion rotational distributions for near-threshold photoionization of H_2O

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In a recent paper, we reported on the rotationally resolved threshold photoionization of H_2O into the (000), (100), and (010) vibrational levels of the $\tilde{X}\,^2B_1$ ground ionic state of H_2O^+.[1] High resolution (~ 1 cm^{-1}) threshold photoelectron spectra for both room temperature and jet-cooled (15 K) H_2O were obtained by the pulsed field ionization (PFI) method in conjunction with a coherent VUV radiation source. The spectra could be readily assigned to two types of rotational photoionization transitions, corresponding to specific changes in the asymmetric top angular momentum projection quantum numbers K_a and K_c. Most of the stronger lines can be classified as type c rotational transitions ($\Delta K_c = 0$, $\Delta K_a = \pm 1$) but type a ($\Delta K_c = \pm 1$, $\Delta K_a = 0$) transitions are also clearly evident, particularly in the jet-cooled spectra. The appearance of type a transitions with $\Delta K_a = 0$ is in variance with the predictions of a multichannel quantum defect theory (MQDT) analysis of photoionization of asymmetric top molecules by Child and Jungen.[2] These authors predict that photoionization will only involve a subset of type c transitions with $|\Delta K_a| = |K_a^+ - K_a^i| = 1$ and $|\Delta N| = |N_+ - N_i| \leqslant 1$, where N is the total angular momentum exclusive of spin. These limits on the changes of core angular momenta arise from the assumption that the $1b_1$ molecular orbital can be described exclusively in terms of an atomic p_y orbital with both l and its body fixed projection $|\lambda|$ equal to one. Although the authors characterize these as propensity rules, they are predicted to become stronger as the upper state approaches the Hund's case (d) limit, i.e., as the Rydberg levels converge to the ionization threshold. More recently, Gilbert and Child[3] have presented a model based on field-induced autoionization in an effort to explain the appearance of type a transitions in the threshold spectra of H_2O. Although such rotational autoionization processes could give rise to the appearance of rotational final states which are nominally forbidden by optical selection rules, the specific application to H_2O also invokes an atomiclike description of photoexcitation from the $1b_1$ molecular orbital.

In this work, we report the results of an *ab initio* calculation of the near-threshold photoelectron spectrum of water into the $\tilde{X}\,^2B_1$ (000) ground ionic state. In this calculation, no assumptions concerning the atomic character of the initial and final states are made and the continuum is calculated in the full anisotropic potential of the ion core. Both type a and type c rotational photoionization transitions are predicted and the intensities are in excellent agreement with the observed PFI results. Analysis of the partial wave distribution shows that type a transitions occur with the ejection of nearly pure p wave continua at near-threshold energy. These calculations emphasize the importance of the nonspherical nature of the molecular ion potential which can scatter the photoelectron into various angular momentum components.

The threshold photoelectron spectrum of the $\tilde{X}\,^2B_1$ (000) state of H_2O^+ presented here was obtained by the PFI method which is a variant of the zero-kinetic-energy (ZEKE) technique developed by Müller-Dethlefs, Schlag, and co-workers.[4] The PFI technique takes advantage of the continuity of oscillator strength for absorption into Rydberg levels 1–2 cm^{-1} below an ionization threshold and for photoionization just above that threshold.[5,6] Tunable narrowband (0.7 cm^{-1}) VUV radiation in the range 98.3–98.1 nm required for one-photon photoionization into the (000) level was produced by third harmonic generation of UV light in a free-jet expansion of argon gas. The overall linewidth of ~ 2 cm^{-1} (FWHM) is a convolution of the VUV bandwidth and the Stark shift induced by the pulsed electric field (0.3 V/cm). Rotationally cold water was prepared in a skimmed molecular beam formed from the expansion of a 200 Torr mixture of 10% water in argon through a pulsed valve with a 0.5 mm nozzle. A complete account of the experimental details can be found elsewhere.[1,7]

In our derivation of the rotational selection rules for photoionization of water, we have used Hund's case (b) to represent the ground states of both H_2O and H_2O^+. The molecular z axis is chosen to be the C_2 symmetry axis and the x axis is in the plane of the molecule (or ion). Thus, the body-fixed axes x, y, and z coincide with the a, c, and b axes, respectively. With these choices, it can be shown that the bound-free dipole matrix element can be written as[8]

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$$\langle f|\mu|i\rangle = \sum C[1+(-1)^{\Delta N+\Delta p+l+1}] \times \begin{pmatrix} N_t & 1 & l \\ -K_t & \mu & \lambda \end{pmatrix} \left[\begin{pmatrix} N_+ & N_i & N_t \\ -K_+ & K_i & K_t \end{pmatrix} + (-1)^{p_+} \begin{pmatrix} N_+ & N_i & N_t \\ K_+ & K_i & K_t \end{pmatrix} \right], \quad (1)$$

with $\Delta N = N_+ - N_i$, and $\Delta p = p_+ - p_i$. In Eq. (1) C is related to the electronic transition dipole moment given in Ref. 8, N_+ and N_i are the total angular momenta (exclusive of spin) for the ion and ground state H_2O, respectively, K_+ and K_i their projections on the z axis, p_+ and p_i the parities of their rotational wave functions, N_t the angular momentum transfer, l an angular momentum component of the photoelectron matrix element, λ its projection along the molecular z axis, and μ the light polarization index in the molecular frame. With the symmetry properties of the asymmetric top[9] and our choice of the molecular axes, it can be shown that ΔK_a is even (odd) when $\Delta N + \Delta p$ is even (odd). Thus, using this relationship and Eq. (1) we obtain the selection rules

$$\Delta K_a + l = \text{odd}, \quad (2)$$

and

$$\Delta K_b = \mu + \lambda, \quad (3)$$

with $\Delta K_a = K_a^+ - K_a^i$ and $\Delta K_b = K_b^+ - K_b^i$, where K_a and K_b are the projections of the total angular momentum (except spin) along the a and b axes, respectively. In C_{2v} symmetry,[9] the x, y, and z components of the dipole moment operator belong to the b_2, b_1, and a_1 irreducible representations, respectively. There are three corresponding dipole-allowed continuum channels ka_2, ka_1, and kb_1 for photoionization of an electron from the $1b_1$ orbital of the ground state H_2O, leading to the $\tilde{X}\,^2B_1$ ground state of H_2O^+. In this case, even λ and odd μ are associated with the ka_1 and ka_2 channels, whereas odd λ and even μ are associated with the kb_1 channel. Therefore $\lambda + \mu$ is always odd for all allowed transitions. Thus, from Eq. (3) we obtain

$$\Delta K_b = \text{odd}. \quad (4)$$

From Tables II and IV of Ref. 9, it can be shown that $\Delta K_a + \Delta K_c$ is even (odd) when ΔK_b is even (odd). Hence, we have

$$\Delta K_a + \Delta K_c = \text{odd}. \quad (5)$$

Equations (2) and (5) show that both type c (ΔK_a = odd and ΔK_c = even) transitions, which are associated with even l partial waves, and type a (ΔK_a = even and ΔK_c = odd) transitions, which are associated with odd l's, are allowed. However, type b transitions are forbidden.

In our calculations of the rotationally resolved threshold photoelectron spectra for H_2O, the ground state wave function is obtained at the Hartree–Fock level at the known equilibrium geometry ($R_{O\text{-}H} = 1.8085$ a.u. and $\Theta_{H\text{-}O\text{-}H} = 104.50°$).[10] For the final state, we use the frozen-core Hartree–Fock approximation, in which the ion-core orbitals are assumed to be identical to those of the initial state of H_2O and the photoelectron orbitals are obtained as solutions of the static-exchange Hamiltonian of the ion.[11] These photoelectron (continuum) orbitals are obtained numerically using the iterative Schwinger variational method.[12,13] Furthermore, we assumed that no spin exchange takes place during the supersonic expansion of an equilibrated water sample. Therefore a ratio of 3:1 is assumed for ortho to para water. Boltzmann distributions are calculated separately for the ortho and para species at 15 K.

Figure 1 shows results of *ab initio* calculations of the rotationally resolved threshold photoelectron spectra along with the measured PFI spectra for the $\tilde{X}\,^2B_1$ (000) ground state of H_2O^+. A photoelectron kinetic energy of 50 meV is assumed in the calculation. The calculated spectra are convoluted with a Gaussian detection function having a full width at half-maximum of 2 cm^{-1}. The agreement between the calculated and experimental spectra is very encouraging. These spectra show both type a and type c transitions in contrast to the prediction of Child and Jungen[2] of type c transitions only. Type a transitions are due to odd angular momentum components of the photoelectron matrix element which arise primarily from the torques exerted by the molecular ion potential. Since the $1b_1$ orbital of the $\tilde{X}\,^1A_1$ ground state of H_2O has almost pure p (99.7%) character, predominant even partial wave contributions to the photoelectron matrix element, i.e., $2p \rightarrow ks$, and kd transitions, leading to type c transitions, are expected in an atomiclike picture. Interestingly, close comparison of calculated vs experimental intensities shows a slightly systematic asymmetry between rotational transitions with $\Delta N = -1$ ("P" branch) and $\Delta N = +1$ ("R" branch). Similar effects in which anomalous intensity appears in photoionizing transitions with negative changes in core angular momentum have been seen in many other cases.[14,15] Its source has been traced in several definitive cases to a rotational coupling mechanism similar to that proposed by Gilbert and Child.[3,15] Thus some evidence for such coupling can be detected in the rotationally resolved photoionization spectra of H_2O for both type a and type c transitions. However, the present work clearly shows that it is not an essential feature for the appearance of type a transitions.

Figure 2 shows the photoelectron angular distributions for the specific rotational ion levels shown in Fig. 1. Following the selection rule of Eq. (2), the angular distributions for type a transitions ($1_{01} \rightarrow 0_{00}$, $0_{00} \rightarrow 1_{01}$, $1_{01} \rightarrow 2_{02}$, and $1_{11} \rightarrow 2_{12}$) have almost pure p wave contributions to the photoelectron matrix element. Interestingly, several of the type c transitions $1_{10} \rightarrow 0_{00}$, $1_{01} \rightarrow 1_{11}$, and $1_{10} \rightarrow 2_{20}$ have almost pure s wave contributions whereas the recent model calculations of Child and Jungen[2] and Gilbert and Child[3] using atomic analogies consider exclusively d wave final states for type c transitions. The $1_{01} \rightarrow 2_{11}$, $0_{00} \rightarrow 2_{12}$, and $1_{01} \rightarrow 3_{13}$ transitions have about equal s and d wave contributions.

These calculations emphasize the importance of the nonspherical nature of the molecular ion potential which

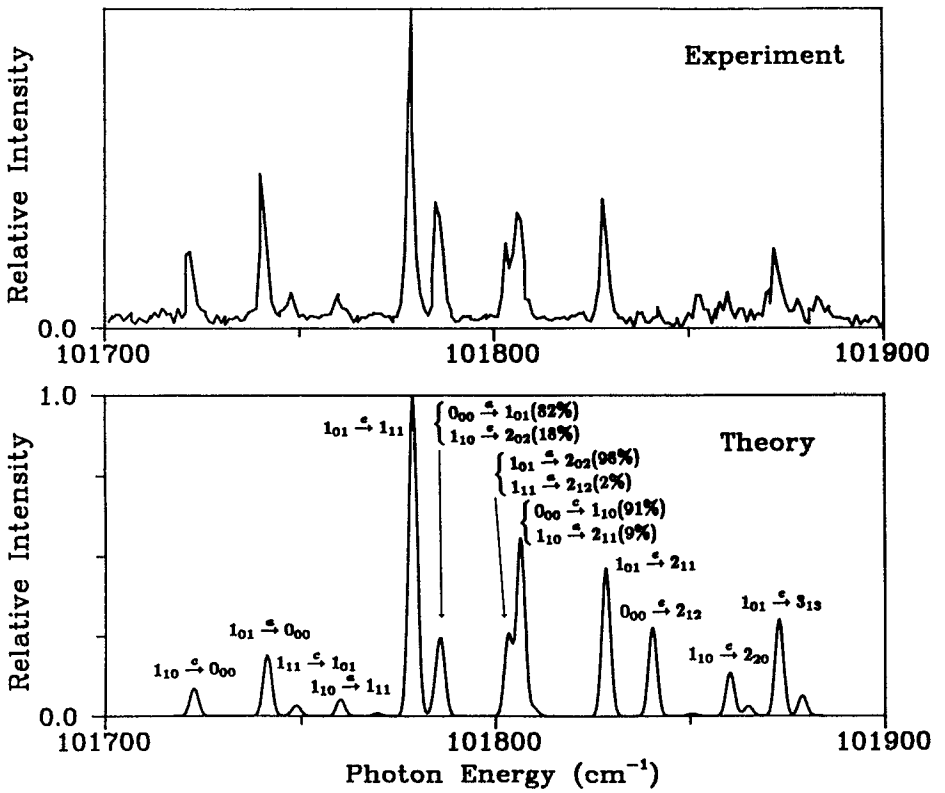

FIG. 1. Experimental (top) and calculated (bottom) ion rotational distributions for photoionization of the $1b_1$ orbital of the $\tilde{X}\,^1A_1$ ground state of H_2O. The *a* and *c* labels indicate type *a* and type *c* transitions, respectively.

can scatter the photoelectron into angular momentum channels that differ significantly from expectations based on atomiclike selection rules. Such nonatomic-like behavior of the molecular photoelectron matrix element has been extensively documented in previous experimental and theoretical studies involving resonance enhanced multiphoton ionization of excited Rydberg states of diatomic molecules.[16]

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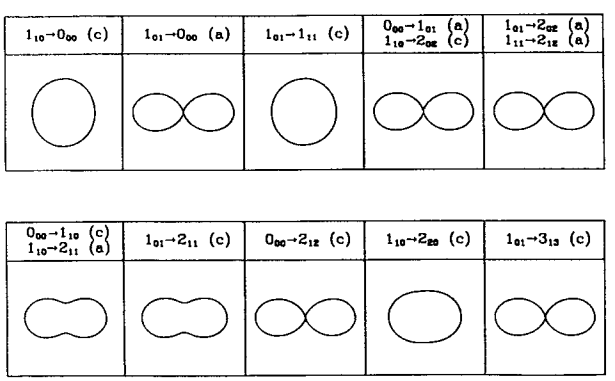

FIG. 2. The calculated photoelectron angular distributions associated with specific rotational levels of Fig. 1. The *a* and *c* labels indicate type *a* and type *c* transitions, respectively. $\theta = 0°$ is vertical.

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[1] R. G. Tonkyn, R. T. Wiedmann, E. R. Grant, and M. G. White, J. Chem. Phys. **95**, 7033 (1991).
[2] M. S. Child and Ch. Jungen, J. Chem. Phys. **93**, 7756 (1990).
[3] R. D. Gilbert and M. S. Child, Chem. Phys. Lett. **187**, 153 (1991).
[4] K. Müller-Dethlefs and E. W. Schlag, Annu. Rev. Phys. Chem. **42**, 109 (1991).
[5] G. Reiser, W. Habenicht, K. Müller-Dethlefs, and E. W. Schlag, Chem. Phys. Lett. **152**, 119 (1988).
[6] R. G. Tonkyn, J. W. Winniczek, and M. G. White, Chem. Phys. Lett. **164**, 137 (1989).
[7] R. G. Tonkyn and M. G. White, Rev. Sci. Instrum. **60**, 1245 (1989).

[8] M.-T. Lee, K. Wang, V. McKoy and L. E. Machado (to be published).
[9] R. S. Mulliken, Phys. Rev. **59**, 873 (1941).
[10] G. Herzberg, *Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules* (Van Nostrand, New York, 1966).
[11] R. R. Lucchese, G. Raseev, and V. McKoy, Phys. Rev. A **25**, 2572 (1982).
[12] M. Braunstein, V. McKoy, L. E. Machado, L. M. Brescansin, and M. A. P. Lima, J. Chem. Phys. **89**, 2998 (1988).
[13] L. E. Machado, L. M. Brescansin, M. A. P. Lima, M. Braunstein, and V. McKoy, J. Chem. Phys. **92**, 2362 (1990).
[14] R. T. Wiedmann, R. G. Tonkyn, E. R. Grant, and M. G. White, J. Chem. Phys. **95**, 746 (1991).
[15] R. G. Tonkyn, R. T. Wiedmann, and M. G. White, J. Chem. Phys. (in press).
[16] See, for example, S. N. Dixit, D. L. Lynch, and V. McKoy, Phys. Rev. A **32**, 1267 (1985); H. Rudolph, V. McKoy, and S. N. Dixit, J. Chem. Phys. **90**, 2570 (1989); S. W. Allendorf, D. J. Leahy, D. C. Jacobs, and R. N. Zare, *ibid.* **91**, 2216 (1989); E. de Beer, C. A. de Lange, J. A. Stephens, K. Wang, and V. McKoy, *ibid.* **95**, 714 (1991); K. Wang, J. A. Stephens, and V. McKoy, *ibid.* **95**, 6456 (1991); K. Wang and V. McKoy, *ibid.* **95**, 4977 (1991); **95**, 7872 (1991); **95**, 8718 (1991).